

DATA EVALUATION REVIEW 8

- I. Study Type: Rotational Crop Accumulation, Confined (165-1)
- II. Citation:

STUDY 1

Schwalbe-Fehl, M., Stumpf, K. Reply to the EPA Environmental Fate Data Review Dated October 14, 1988. developed by Hoechst AG, Frankfurt am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 12/30/89. Received EPA 5/31/89 under MRID # 413231-25.

STUDY 2

Schwalbe-Fehl, M., Stumpf, K. Hoe 039866-¹⁴C Residue Determinations and Metabolism in Rotational Crops Sown 120 Days After Treatment of Soil. performed by Hoechst AG, Frankfurt am Main, Federal Republic of Germany, submitted by Hoechst Celanese Corporation, Somerville, NJ, USA. dated 12/30/89. Received EPA 5/31/89 under MRID # 413231-26.

- III. Reviewer:

Typed Name: E. Brinson Conerly
Title: Chemist, Review Section 2
Organization: EFGWB/EFED/OPP

- IV. Conclusions:

STUDY 1

Most, but not all, of the previous EFGWB comments have been satisfactorily answered, but the study has been replaced by more recent ones. We note that control plants were said to have taken in radioactive CO₂ from experimental plants kept near them. This would certainly have made interpretation of the results more difficult.

STUDY 2

The analytical method is somewhat less sensitive than is desirable. It will be acceptable if the applicant can demonstrate that it is the best available at this time. The study will then become fully acceptable, but can only support a use rate approximately half the maximum label rate. A 4 month (120 day) interval after the final treatment appears to be appropriate for planting of rotational crops based on these data. The description of the formulation is not readily apparent in EFGWB files.

- V. Materials and Methods:

STUDY 1 -- n.a.**STUDY 2**

test formulation -- 17.9% active ingredient, spec. act. 4.7 MCi/gm, formulated from 7.5 mg 99.6% radiopure HOE 039866-¹⁴C (labelled in the 3 and 4 positions), 62.6 mg unlabelled HOE 039866, and 320.0 "Blank Formulation" [designated by a company code, but not otherwise described]

DER 8-1



spray mixture -- 390 mg test formulation plus 35 ml H₂O
test protocol -- spray mixture was applied at 0.87 ppm a.i. to soil which had been aged 2 mos. in a container 1.0 m x 0.7 m x 0.5 m. d. Rotational crops of radish, spinach, wheat, and carrots were sown 120 days after treatment. Prior to sowing, the upper layer of the soil was loosened, but weeds which were present at the time of treatment were not removed. They covered approximately 1/3 of the surface. Growing conditions were as follows:

sowing -- April 14, 1987
greenhouse -- April 14 - 20, 1987
outdoors but under a roof -- April 20 - 27, 1987
outdoors without a roof -- April 27 - Sept. 8, 1987

Temperature and irrigation details are attached.

sampling protocol -- mature crops were harvested as follows:

radishes -- 43 days after sowing (163 days after treatment)
spinach -- 43 days after sowing
wheat and carrots -- 147 days after sowing

analytical methods -- level of quantitation (loq) 0.0007 - 0.04 ppm

plant samples -- homogenization, followed by water extraction. Clean-up of the concentrated extracts was by (1) methanol extraction, or (2) anion exchange chromatography followed by 10% formic acid elution, or (3) dialysis. Purified extracts were subjected to HPLC/TLC or derivitization followed by GC/MS. Total radioactivity was determined by LSC. Samples were analyzed within one week, but the quantity and nature of residues were stable for at least 6 months (data not included). There were no data presented indicating the level of recovery from fortified samples.

soil samples -- repeated extraction with hot distilled water. The concentrated water extract was analyzed for radioactivity by LSC. Total and unextracted radioactivity were determined by combustion followed by LSC. There were no data presented indicating the level of recovery from fortified samples. Total radioactivity was determined by combustion, and was relatively constant throughout. There were no data presented indicating the level of recovery from fortified samples. Recoveries in various fractions (extracted, bound, etc.) ranged from 94.1 to 104.5% of total, with no evidence of time dependency.

VI. Study Author's Results and/or Conclusions:

STUDY 1 -- [Reply to comment of previous review]

Confined 30 days study:

Soil was treated with a small hand-spraying device. Direct mixing of pesticide into the soil would also have been practicable ... but is not usually carried out in agricultural practice. ... Spray application was preferred, ... [but] generally results in greater variations of the soil concentrations directly after treatment ... especially if only few soil samples are taken... One special circumstance probably enhanced the variability of the soil concentrations in the confined 30 days study: weeds covered the soil surface of the test container to approx. [sic] one third of the container surface ... [and] ... were not removed prior to the treatment. In agricultural practice, HOE 039866 is never applied to bare soil but only to soil covered with weeds, because ... [it] ... acts only via contact with the green parts of the weeds. As the damaged weeds were kept in the container throughout the study, the increase of the radioactivity concentrations in the

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soil at later sampling dates is understandable. Although this procedure probably led to an increased variability of soil residues, it simulates what generally happens in practice.

...It was impossible to collect volatile degradation products because of the size of the container. ... [This] is generally not necessary ... because the results can be provided from the aerobic soil degradation laboratory studies which are carried out with the same soil ... It was observed, however, that soil degradation in containers was slower than in the corresponding standard laboratory degradation studies. Consequently the confined crop rotation studies provide the worst case scenarium [sic] for soil degradation.

From the results of the control plants kept in the same room as the treated ones, it can be clearly proved that CO₂ from soil was evolved; otherwise control plants could not contain radioactive residues at the measured level.

The study was carried out using the normal water-soluble concentrate formulation SL18 which was used in all studies that had to be carried out with formulated material. Consequently, a further description of the formulation is not necessary.

Plants were not sampled immature because neither radishes nor spinach, carrots or wheat are used as feed or food items when immature.

Fortifications of soil samples were not carried out because the use of radiolabeled material allowed the determination of recoveries per se. Moreover, the extraction and clean-up procedure for soil samples was identical [sic] with that of the routine residue method which is routinely validated by determining the recovery of fortified soil samples.

Confined 120 days Study:

Residues in soil were only characterized at the time of harvest. This deficiency is overcome by the new 120 days confined crop rotation study which is submitted together with this answer.

The one unidentified degradate at day 158 ... proved to be HOE 064619 after GC-MS analysis and comparison with the authentic reference compound. Its appearance in soil was ... confirmed in the new 120 days ... study.

Plant and soil samples were always stored deep frozen (-20°C) until analysis.

[Blank formulation, immature plant sampling, and fortification of soil samples are discussed under the 30 day study.]

STUDY 2

Results

Plant residues (details attached)

All plant samples except those of wheat contained less than 0.04 mg/kg (0.04 ppm) and were not investigated further. Following clean-up, the only identifiable metabolite in the extracts was HOE 061517. Most radioactivity was associated with cellulose or hemicellulose. From 11 to 20 % (0.01 to 0.02 ppm) of the residues were identified as HOE 061517.

Soil residues (details attached)

Significant soil residues were only found in the upper 5 cm. At day 0, total residues were 0.745 mg ai equiv./kg (86% of applied). The 5-10 cm layer contained residues above the limit of quantification (0.039 mg ai equiv/kg = 39 ppb) only at 120 days after treatment.

Day 0 extracts only contained HOE 039866. HOE 061517 and, later, HOE 064619 were detected in subsequent samples. HOE 039866 was completely undetected by days 163 and 267. Calculated half-lives are 20 days for HOE 039866, 45 days for HOE 061517, and 30 days for HOE 064619. HOE 039866 is degraded to significant amounts of CO_2 .

Conclusions

The nature of the residues in rotated crops is fully understood. Incorporation of most of the recovered radioactivity in cellulose and hemicellulose indicates complete metabolism of parent to degradates such as CO_2 or those degradates shortly before it such as succinic or acetic acid [i.e., it becomes part of the "carbon pool" -- EBC]. Plants then use it to form glucose, fatty and amino acids, cellulose, etc, which are found in all parts. HOE 061517 (3-methylphosphinicopropionic acid) is the only residue of concern in plants.

Taking into account that soil degradation depends largely on growing conditions (temperature, moisture, etc.), calculated half-lives are in good agreement with those from the aerobic soil metabolism study: 3 - 10 days for HOE 039866, 7 - 22 days for HOE 061517, and 18 - 30 days for HOE 064619.

VII. Reviewer's Comments:

STUDY 1 -- see section IV, "Conclusions", above.

STUDY 2

- 1) The investigator's conclusions are supported for the rate tested, which is approximately half the maximum label rate for a single application. However, this does not provide information on the maximum use rate.
- 2) The study is an "outdoor confined" study, which could be expected to yield results more closely related to those observed in a true field study.
- 3) Direct uptake of the parent and closely related degradates seems to be insignificant at the level tested.
- 4) The HPLC method appears to separate the parent and major degradate satisfactorily. The sensitivity (limit of quantitation or loq) as calculated by the investigator is 0.04 ppm for soil, rather than 0.01. This value for the loq in soil is based on 30 counts (99% confidence level) above the mean of the control soil ("background") value for the LSC analysis. Sensitivities for the various plant material ranged from 0.7 to 27 ppb. Some of these do not meet the "10 ppb" criterion established by EFGWB. The guidelines mention 0.01 ppm as desirable, but not an absolute requirement. The investigator may be able to demonstrate that the method is the best available, and it would then be fully acceptable.
- 4) Soil bound residues increased over time, to ca. 70% of the original material at day 267.
- 5) HOE 061517 constituted 90% of extractable material in the top 5 cm of soil at day 267. Although this was not a soil dissipation study, if

additional soil analyses were done for HOE 061517, EFGWB would like them as part of the record. This degradate is somewhat persistent, and is therefore a matter for attention.

- 6) The presentation of data is less than ideal, since pertinent information is given in several tables, rather than in one.

VIII. CBI Information Addendum: attached